

CARBON-13 NUCLEAR MAGNETIC RESONANCE OF STRAINED ORGANIC MOLECULES: III ESTIMATES OF STERIC EFFECTS.

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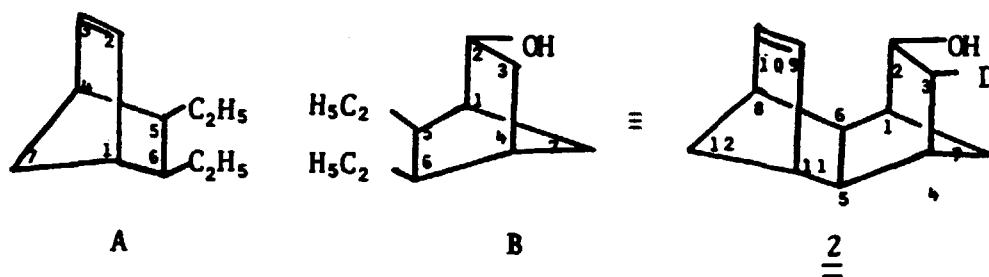
Carbon-13 NMR Spectroscopy has found ample use in the study of cyclic organic molecules. We have analysed a series of highly strained polycyclic hydrocarbons¹ and found that their chemical shifts can be predicted to a reasonable degree. Derivations from expected values can thus be attributed to a number of effects such as electronegativity, hybridization, steric compression, etc.

In compounds of the endo-endo tetracyclo {6.2.1.1^{3,6}.0^{2,7}} - type, such as 1, norbornane, norbonene and



their derivatives are used to estimate chemical shifts. In the unsaturated alcohol 2, it was shown¹ that steric factors can account for shifts on the order of 1,5-3,0 ppm for carbons on the ethano bridges (see Table 1). For carbons on the methano bridges, however, steric compression alone cannot be responsible for the difference between chemical shifts in 2 and the corresponding carbon atoms in endo 2-methyl bicyclo {2.2.1} heptene, 3 and endo-2-ethyl bicyclo {2.2.1} heptan-exo-ol 4. Deviations for shifts of carbons on the junction of the two norbornyl rings (i.e. C₅ and C₆) apparently did not seem to arise from steric factors alone either.

Table I - Estimated VS Assigned CMR chemical shifts.

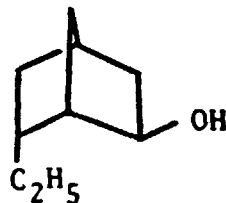


CARBON	ESTIMATED CHEMICAL SHIFT (PPM)	OBSERVED CHEMICAL SHIFT (PPM)	(OBS - EST)
1	48,5	48,0	-0,5
2	67,4	70,5	+3,1
3	35,0	37,0	+2,0
4	39,8	38,9	-0,9
5	48,4	44,4	+4,0
6	46,5	44,2	-2,3
7	37,8	43,6	+5,8
8	46,4	46,5	+0,1
9	134,2	131,9	-2,3
10	134,2	132,5	-1,7
11	46,4	46,4	0,0
12	51,4	58,8	+7,4

A - Estimated from endo-5 methylnorbonene. Chemical shifts of alkyl carbons adjusted from Ethyl-Methyl increments.

B - Estimated from endo-2 ethylbicyclo {2.2.1} Heptane and Bicyclo {2.2.1}-exo-ol^{1b}

1

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As 2 serves as a basis for interpreting chemical shifts on other tetracyclic compounds of this type, it was necessary to determine the exact nature of effects that influence chemical shift values and the extent of their respective contributions. We thus decided to compare our results with those for a series of compounds which would permit us to examine the validity of bicyclic compounds 3 and 4 as a basis for estimating shifts in tetracyclic analogs and to assess the steric contribution relative to carbons 5, 6, 12 and 7 in 2.


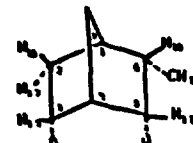
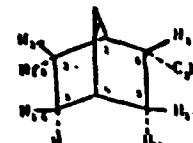
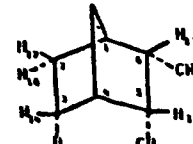

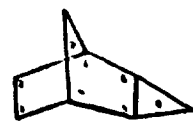
Experimental

Preparation of compounds and analysis of carbon-13 NMR spectra have been described in previous communications.^{1a} Bond distances and angles were obtained from optimized geometries using force field calculations.² These were run on a Burroughs 6900 computer using a modified version of MM2 (QCPE 395).³

Results and Discussion

Using norbornyl compounds as a basis for chemical shifts, bicyclic, tricyclic and tetracyclic derivatives are compared in Table II. Our main interest lay in the estimation of magnitudes of steric crowding effects and comparisons were selected so as to compensate, as far

TABLE II - Chemical Shifts, Bond Lengths, Bond Angles, Van der Waals Interactions.

COMPOUNDS	CHEMICAL SHIFTS 13 C (PPM)	BOND LENGTHS (ANGSTROM)	BOND ANGLES (°)	VAN DER WAALS INTERACTIONS
	C(1) → 37,3 C(2) → 30,6 C(3) → 30,7 C(4) → 37,3 C(5) → 30,6 C(6) → 30,6 C(7) → 35,2 REF. 6	C(1) - C(7) → 1,5372 C(2) - C(3) → 1,5401 C(4) - C(7) → 1,5372 C(5) - C(6) → 1,5401	C(1) - C(7) - C(4) 92,524	H(9) - H(11) → 0,3410 H(10) - H(12) → 0,5145 H(14) - H(16) → 0,3410 H(15) - H(17) → 0,5145
	C(1) → 42,1 C(2) → 22,3 C(3) → 30,6 C(4) → 30,1 C(5) → 30,9 C(6) → 34,5 C(7) → 40,7 CH ₃ → 17,5 REF. 6	C(1) - C(7) → 1,5398 C(5) - C(6) → 1,5418 C(7) - C(4) → 1,5372	C(1) - C(7) - C(4) 92,464	H(10) - H(11) → 0,5571 H(14) - H(17) → 0,3259 H(15) - H(16) → 0,5286 H(12) - H(14) → 0,2118
	C(1) → 40,0 C(2) → 22,6 C(3) → 30,6 C(4) → 37,6 C(5) → 37,5 C(6) → 42,0 C(7) → 40,3 CH ₂ → 26,2 CH ₃ → 13,4 REF. 7	C(1) - C(7) → 1,5402 C(5) - C(6) → 1,5422 C(7) - C(4) → 1,5365	C(1) - C(7) - C(4) 92,369	H(11) - H(13) → 0,6541 H(12) - H(15) → 0,2108 H(15) - H(18) → 0,3010 H(10) - H(17) → 0,5318
	C(1) → 43,1 C(2) → 21,0 C(3) → 21,0 C(4) → 43,1 C(5) → 34,0 C(6) → 34,0 C(7) → 39,7 CH ₃ → 11,0 REF. 6	C(1) - C(7) → 1,5395 C(5) - C(6) → 1,5462 C(7) - C(4) → 1,5395	C(1) - C(7) - C(4) 92,369	H(11) - H(12) → 0,7920 H(14) - H(17) → 0,5476 H(15) - H(16) → 0,3229
	N.A.	C(1) - C(7) 1,5434 C(5) - C(6) 1,5507 C(7) - C(4) 1,5443	C(1) - C(7) - C(4) 92,763	H(13) - H(14) → 1,2410 H(16) - H(19) → 0,5150 H(14) - H(20) → 1,3857 H(17) - H(18) → 0,3777 H(17) - H(30) → 0,7142 H(18) - H(21) → 0,8081
	C(1) → 36,6 C(2) → 23,1 C(3) → 23,1 C(4) → 36,6 C(5) → 26,8 C(6) → 26,8 C(7) → 33,3 C(8) → 17,7 REF. 9	N.A.	N.A.	N.A.

(Continued) TABLE II - Chemical Shifts, Bond Lengths; Bond Angles, Van der Waals Interactions.

	C(1) - 39,6 C(2) - 23,8 C(3) - 23,8 C(4) - 39,6 C(5) - 45,5 C(6) - 40,3	C(7) - 41,3 C(8) - 18,7 C(9) - 18,7 REF. 10	C(1) - C(7) - 1,5417 C(5) - C(6) - 1,5550 C(7) - C(4) - 1,5416	C(1) - C(7) - C(4) 92,551	H(11) - H(12) - 0,3848 H(14) - H(16) - 0,3027 H(15) - H(17) - 0,5671 H(14) - H(22) - 0,7169
	C(1) - 41,5 C(2) - 23,1 C(3) - 23,1 C(4) - 41,5 C(5) - 45,5 C(6) - 23,1	C(7) - 43,3 C(8) - 27,0 C(9) - 28,7 C(10) - 27,0 REF. 11	C(1) - C(7) - 1,5432 C(5) - C(6) - 1,5426 C(7) - C(4) - 1,5432	C(1) - C(7) - C(4) 92,879	H(12) - H(13) - 0,7062 H(15) - H(17) - 0,7913 H(17) - H(21) - 0,6403 H(16) - H(18) - 0,5652
	C(1) - 39,8 C(2) - 41,8 C(3) - 74,2 C(4) - 49,3 C(5) - 43,3 C(6) - 47,2	C(7) - 20,6 C(8) - 32,0 C(9) - 27,9 C(10) - 31,7 REF. 12	N.A.	N.A.	N.A.
	N.A.	N.A.	C(5) - C(6) - 1,5392 C(11) - C(12) - 1,5515 C(8) - C(12) - 1,5199 C(1) - C(7) - 1,5515 C(4) - C(7) - 1,5499	C(8) - C(12) - C(11) 92,982 C(1) - C(7) - C(4) 92,983	H(15) - H(16) - 0,6563 H(25) - H(28) - 1,6713 H(26) - H(29) - 1,1210
	N.A.	N.A.	C(5) - C(6) - 1,5494 C(11) - C(12) - 1,5551 C(8) - C(12) - 1,5551 C(1) - C(7) - 1,5472 C(7) - C(4) - 1,5402	C(11) - C(12) - C(8) 93,825 C(1) - C(7) - C(4) 93,000	H(15) - H(16) - 0,5872 H(25) - H(28) - 0,5861
	C(1) - 48,0 C(2) - 70,5 C(3) - 37,0 C(4) - 38,9 C(5) - 44,4 C(6) - 44,2	C(7) - 43,6 C(8) - 46,5 C(9) - 131,9 C(10) - 132,5 C(11) - 46,4 C(12) - 58,8	C(5) - C(6) - 1,5496 C(11) - C(12) - 1,5552 C(8) - C(12) - 1,5552 C(1) - C(7) - 1,5408 C(7) - C(4) - 1,5496	C(11) - C(12) - C(8) 93,831 C(1) - C(7) - C(4) 93,036	H(16) - H(21) - 0,5868

possible, for any other type of contribution.

Relevant distances, angles and non-bonded interactions are also shown in table II. Interatomic distances are used to verify if carbon - carbon bonds are stretched or compressed relative to other structures. The importance of steric interactions between non-bonded atoms is inferred from comparisons of the relative magnitudes of Van der Waals type energies (only the most significant ones appear in table II). Optimized geometries are used qualitatively since there are still discrepancies between data on norbornyl-type compounds obtained from force-field calculations and that from other physical methods.⁴

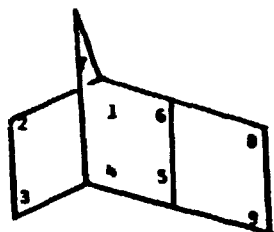
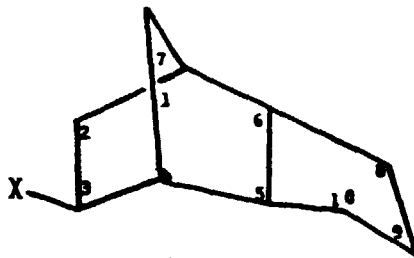
Based on norbornane the main steric effects on the C₅-C₆ bond, which correspond to C₅-C₆ in 2 arise from interactions between pairs of exo and endo hydrogens on C₅ and C₆, H₁₀-H₁₂ and H₉-H₁₁ respectively. Substituting a hydrogen atom on one of these two carbon atoms by a methyl group, reduces this interaction but introduces new steric crowding between either the syn hydrogen on C₇ (for the exo case) or the endo-hydrogen on C₂ for the endo case), since the interaction between hydrogens on C₅ and C₆ is mainly responsible for upfield shifts, with its removal C₆ resonances are shifted to lower fields. In terms of geometry, it appears that the substituent introduces additional crowding with the exo-or endo-hydrogens and that this effect is compensated for by pushing these groups further apart, stretching the C₅-C₆ bond and bringing the remaining pairs of protons into closer contact (hence the upfield shifts observed with more crowded geometries or larger groups).

As a second substituent is introduced, interactions by hydrogens on carbons 5 and 6 are further reduced and the respective interactions of these substituents with hydrogens on C₂ are increased accordingly. As for C₇ it is noteworthy that the introduction of one endo-5-methyl substituent shifts the absorption downfield and that this effect is smaller for two endo methyl substituents than it is for one.

In the presence of a ring instead of an alkyl group, the same type of effect on C₂ and C₇ can be observed. A downfield shift is observed for C₇ on endo-substitution and, for the cyclopropyl ring, this effect is considerable. The same trend is followed by the corresponding norbornene analogs.

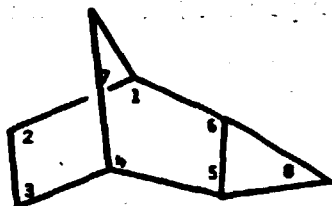
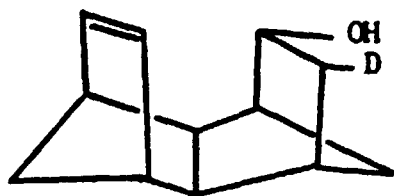
Thus, the "deviations" observed for C₅ and C₆ in 2 are probably, to a large extent due to a decrease in the interaction of endo-hydrogens on C₅ and C₄ as a result of strain on the respective C₁₁-C₅ and C₃-C₄ bonds to form a new ring (the relative contributions from strain itself and those which have a steric origin are in the same direction and thus are hard to separate. Torsion is probably not playing a very large role since these chemical shifts are very similar to those of the exo-hydroxi-endo-cyclopentyl norbornyl derivative 6b). It is noteworthy, however, that in the absence of any other type of effect, chemical shifts for carbon atoms on the ring junction for 2, 5 and 6a follow the relative order of their respective bond distances.

As for C₃ and C₇ in 2, calculations and comparison with models show that deviations due to steric effects are almost negligible. As force-field calculations do not give reasonable values for the bridge

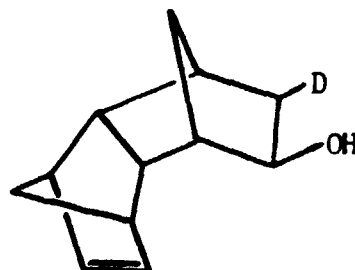
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a: X = H

b: X = OH

72

=



angle,^{4b} it difficult to separate this contribution from that of orbital overlap that was used to explain the large chemical shift differences observed for the bridge carbon in the endo-cyclopropyl norbornyl derivatives 7.⁵ However, the fact that the introduction of an endo-methyl substituent on C₅ or C₆ introduces a down field shift of over 1ppm in C₇ of norbornane and that this effect is still larger in norbornene, increasing further in 6 in which the bridge angle should also be very slightly altered must be due to orbital overlap, even in the case where only σ -bonding is involved.

Acknowledgements: we are grateful to P.Carter and R. Howe for samples of compounds used in this work. J.M. Bernassau e E.R. Maia were of great assistances in adapting the force-field calculations to our computer. Financial assistance was provided by the Conselho Na cional de Desenvolvimento Científico e Tecnológico-CNPq and the Financiadora de Estudos e Projetos - FINEP.

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- b) J.W. de M. Carneiro helped adapt the program to the Burroughs computer at IME and ran some of the calculations, as part of his requirements for a Masters degree, Seção de Química, IME.
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